REMARKS

Claims 1-15 are pending in the application and are at issue.

This response is submitted in accordance with 37 C.F.R. §1.116(a) and §1.116(b) in order to present the rejected claims in a better form for allowance or appeal. The response is necessary to eliminate a rejection under 35 U.S.C. §102(b) and under 35 U.S.C. §103. No amendment accompanies this response. The response should be entered because it places the application in better form for allowance or appeal, and the response does not require further searching or present any new issues.

Claims 1-4, 6, 9-12, 14, and 15 stand rejected under 35 U.S.C. §102(b) as being anticipated by Shimomura et al. U.S. Patent No. 5,210,298 ('298). Claims 5, 7, 8, and 13 stand rejected under 35 U.S.C. §103 as being obvious over the '298 patent in view of GB 1,073,856 (GB '856). Apparently, the basis of these rejections is that the '298 patent discloses a supersaturated solution. Applicants traverse these rejections.

The present invention is directed to a method of preparing a (meth)acrylate polymer by polymerizing a *supersaturated* aqueous solution of a (meth)acrylic salt. As disclosed in the specification at page 2, lines 26-32, a supersaturated solution is a metastable state where *more* of the (meth)acrylate salt is in solution than a fully saturated solution of the salt at thermodynamically stable equilibrium. In particular, a supersaturated solution contains more than 1.01 times the amount of (meth)acrylate salt compared to the thermodynamically stable solution at the same temperature (claim 15). Supersaturated solutions are explained in the attached Exhibit A, i.e., *General Chemistry, 4th Edition* (1972), pages 242-245.

Saturation and supersaturation relate to the concentration of a compound in solution; whereas degree of neutralization relates to the relative amounts of free acid and salt of a compound in solution. The two properties are exclusive of one another.

It must be understood that a supersaturated (meth)acrylate salt solution is different from an overneutralized (meth)acrylate salt solution. Whereas the term "supersaturated" refers to an amount of (meth)acrylate salt in solution greater than that of a saturated solution, the term "overneutralized" refers to the degree of neutralization of the

4

(meth)acrylic acid, i.e., the (meth)acrylic acid is more than 100 mol % neutralized. See specification, page 5, lines 35-38 and page 4, lines 19-24. A (meth)acrylic acid solution can be overneutralized, but not supersaturated, and *vice versa*. For example, a (meth)acrylic acid solution can be neutralized to 102%, but be very dilute, i.e., 1-5%, by weight, for example. Conversely, a (meth)acrylic acid solution can be supersaturated (i.e., a concentration greater than the saturation concentration at a given temperature), yet completely unneutralized. A (meth)acrylic acid solution also can be overneutralized and supersaturated, or neither. The two terms are completely independent of one another.

It also must be noted that supersaturation is related to the temperature of the solution. A solution that is not supersaturated can become supersaturated when the temperature of the solution is reduced. In fact, a standard method of preparing a supersaturated solution is to prepare a saturated or nearly saturated solution, then slowly cool the solution (without causing precipitation) to provide a supersaturated solution. See specification, page 3, lines 31-41, wherein a concentrated solution of sodium acrylate is cooled to provide a supersaturated solution (lines 38-41), as recited in the claims.

The proper bases for a rejection under 35 U.S.C. §102(b) and 35 U.S.C. §103 are set forth in Amendment "A" at pages 5 and 6, incorporated herein by reference. Important aspects of these bases are, for §102(b), a claim is anticipated *only if each and every element* as set forth in the claim is found, either expressly or inherently described, in a single prior art reference and that the identical invention must be shown in as complete detail as is contained in the claim; and for §103, first, there must be apparent reason for a person skilled in the art to combine the known elements in the way the claimed invention does, second, the proposed modification of prior art must have had a reasonable expectation of success determined from the vantage point of the skilled artisan at the time the invention was made, and third, the prior art references must teach or suggest all the limitations of the claims.

It is of prime importance that, contrary to the examiner's contentions, the cited references fail to teach or suggest a *supersaturated* (meth)acrylate solution. Accordingly, the references *fail* to describe, teach, or suggest every claim element, and a rejection under 35 U.S.C. §102(b) or §103 therefore cannot be sustained.

The cited '298 patent discloses a method for the production of a neutralized acrylic acid polymer by neutralizing acrylic acid, including a step of overneutralizing the acrylic acid, then reducing the degree of neutralization to 20 to 100 mol% by the addition of acrylic acid, followed by a polymerization reaction to form the polyacrylate. See '298 patent, column 3, lines 1-18. This process adjusts *only* the degree of neutralization of the acrylic acid, but says nothing about the *concentration* of the acrylic acid in the solution. It is the concentration and solution temperature, not the degree of neutralization, that relates to saturation vs. supersaturation. Alternatively stated, the concentration of the (meth)acrylate is related to the amount of solvent in the composition, not the degree of neutralization. A 75 mole % neutralized (meth)acrylate solution can be unsaturated, saturated, or supersaturated depending upon the amount of solvent, (meth)acrylate salt, and the temperature of the solution.

The examiner specifically relies upon the Examples of the '298 patent to support the anticipation rejection, and especially Example 1. However, differences exist between the '298 patent and the present claims that preclude an anticipation rejection.

In particular, Example 1 of the '298 discloses the following:

(a) providing a 90 to 95 mol% neutralized aqueous acrylic acid solution (column 8, lines 44-50);

(b) adding sodium hydroxide to the solution of (a) to adjust the degree of neutralization to 102%, while adjusting the temperature to 40°C, and aging the resulting solution for 30 minutes (column 8, lines 53-60); then

(c) adding acrylic acid to the aged solution of (b) to reduce the degree of neutralization to 75% (column 8, lines 62-66).
Importantly, the resulting solution contained 37% by weight of the acrylate (column 8, lines 67-68).

A 37% by weight solution of 75 mol% neutralized acrylic acid is *not* supersaturated, but is within the normal concentration of a partially neutralized acrylic acid solution used in the preparation of polyacrylates. See Exhibit B, "Modern Superabsorbent Polymer Technology," F. Buchholz et al., ed. (1998), pages 74-77, submitted concurrently with this response, and particularly page 75, last sentence of the first paragraph, i.e., 30%-

43% monomer concentration for polymerization of partially neutralized monomer. All examples of the '298 patent provide an acrylate solution of 35% to 40%, by weight, *none* of which is supersaturated.

The examiner contends, without any factual support, that the monomer solution of the '298 patent is inherently supersaturated. In paragraph 5 of the Office Action, the examiner provides an analysis that relates to the degree of neutralization. The specification, as noted by the examiner, adds excess acrylic acid that reduces the degree of neutralization to 65-78% *and* provides a supersaturated solution. The cited '298 patent also adds acrylic acid to reduce the degree of neutralization, but provides a 37 weight % solution of acrylate, which is not supersaturated.

Simply adding additional acrylic acid to an overneutralized acrylate solution does *not* inherently lead to a supersaturated solution. A dilute, or very dilute, solution of an overneutralized acrylic acid can have a degree of neutralization reduced by the addition of acrylic acid *without* providing a supersaturated solution. For example, a 1%, by weight, over-neutralized acrylic acid solution can have its degree of neutralization reduced to zero, and still be very, very, far from a saturated, let alone a supersaturated, solution.

The examiner is reminded that to support an inherency theory, the relied upon reference *must*, not may, anticipate the claim, i.e., the missing descriptive matter is *necessarily* present and is so recognized by persons skilled in the art. Further, it is incumbent on the examiner to provide rationale or evidence supporting a contention of inherency. The examiner has failed to meet this burden. See MPEP §2112-2112.02, incorporated herein by reference..

The examiner has neglected the fact that, in the present invention, *additional* acrylic acid also is added to *increase* the *concentration* of the (meth)acrylate solution to greater than saturation. See specification, page 6, lines 2-24, and particularly, lines 12-17. Also, see claim 3, which specifically recites the addition of further acrylic acid, and claim 15. A supersaturated solution of a (meth)acrylate is not taught, suggested, or even addressed or considered in the '289 patent.

The examiner also admitted, in paragraph 12 of the Office Action of September 17, 2008, that the '289 patent *fails* to disclose supersaturation. Contrary to the examiner's other statements, the acrylate concentration used in the '298 patent is standard in the art and it is not a supersaturated solution, expressly or inherently.

It is submitted that the term "supersaturated" recited in the claims cannot be ignored. The present claims do not relate to polymerizing an unsaturated aqueous solution, as disclosed in the '289 patent. The present claims are directed to polymerizing a (meth)acrylate solution of *any* concentration *only* if it is supersaturated. As described in the specification (e.g., page 2, lines 26-32), supersaturation means that the solution is metastable and contains more dissolved salt than would be soluble at a particular temperature. Temperature is a factor in supersaturation, as pointed out in the specification at page 3, lines 31-41. As correctly stated in the Office Action, the '289 patent is *silent* with respect to supersaturation. Consequently, the '289 patent cannot anticipate the present claims, and for failing to teach every limitation of the claims, cannot support a *prima facie* obviousness case rejection under 35 U.S.C. §103.

Because differences exist between the present claims and the '298 patent disclosure, a novelty rejection based on 35 U.S.C. §102(b) cannot be maintained. See MPEP §2131. In addition, it is submitted that the differences between the present claims and the '289 patent are nonobvious differences.

As stated above, the '289 patent is directed to a polymerization method wherein acrylic acid is neutralized, then overneutralized, and allowed to sit, followed by an addition of further acrylic acid to provide a partially neutralized acrylic acid in an amount that is less than the saturation amount. The concentration of partially neutralized acrylic acid solution utilized in the '289 patent (35-40%, by weight) is the standard amount used in the art. This concentration is not a supersaturated concentration. The '289 patent fails to teach or suggest, or even consider or address, polymerizing a supersaturated (meth)acrylate solution, contrary to the assertions of the examiner.

As recognized by the examiner, the '289 patent fails to teach or suggest the content of dimer or inhibitor in the acrylic acid, or the use of a solid acrylate salt. GB '856

fails to overcome the deficiencies of the '289 patent, particularly with respect to polymerizing a supersaturated (meth)acrylate salt solution.

The examiner relies upon GB '856 for a teaching of providing solid sodium acrylate containing a low amount of impurities. Although GB '856 teaches an improved method of preparing sodium acrylate by precipitation from methanol, the reference teaches nothing more. All eight examples of GB '856 show production of a sodium acrylate. The reference contains *no* disclosure with respect to polymerizing the resulting solid sodium acrylate. Accordingly, GB '856 cannot teach or suggest polymerizing a supersaturated *solution* of sodium acrylate. In addition, GB '856 teaches essentially 100% sodium acrylate, as opposed to a partially neutralized (meth)acrylate salt used in the present claims, for example in claim 2. Like the '289 patent, GB '856 fails to teach or suggest a *supersaturated* aqueous monomer solution of a (meth)acrylate salt, as required in claim 13.

In view of the above, a case of *prima facie* obviousness of claims 1-15 over a combination of the '289 patent and GB '856 cannot be established. First, and importantly, the combination of references *fails to teach or suggest* every claimed feature. In particular, neither the '289 patent nor GB '856 teaches polymerization of a *supersaturated* aqueous solution of a (meth)acrylate salt. GB '856 fails to teach *any* polymerization of the solid sodium acrylate, and the '289 patent teaches polymerization of a partially neutralized acrylic acid solution that is not saturated, but in a concentration that is standard in the art.

Second, neither reference alone nor the combination of references provides any apparent reason for a person skilled in the art to modify the teachings in the references and combine the elements in a way the claimed invention does, i.e., there is no apparent reason from the '289 patent and/or GB '856 for a person skilled in the art to provide a supersaturated (meth)acrylic salt solution, and polymerize the supersaturated solution.

Accordingly, it is submitted that claims 1-15 would not have been obvious to a person skilled over a combination of the '289 patent and GB '856, and that the rejection of claims 1-15 under 35 U.S.C. §103 should be withdrawn.

In summary, all pending claims are in a condition for allowance. An early and favorable action on the merits is respectfully requested.

Should the examiner wish to discuss the foregoing, or any matter of form in an effort to advance this application toward allowance, the examiner is urged to telephone the undersigned at the indicated number.

Dated: May 29, 2009

Respectfully submitted,

By _____
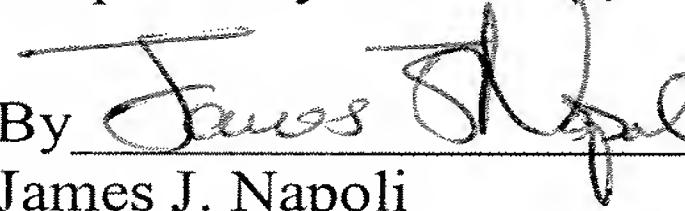
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GENERAL CHEMISTRY

Fourth Edition

Cover design by Oliver Kline. Illustration is based on an x-ray diffraction photograph. See also Figure 10-14.
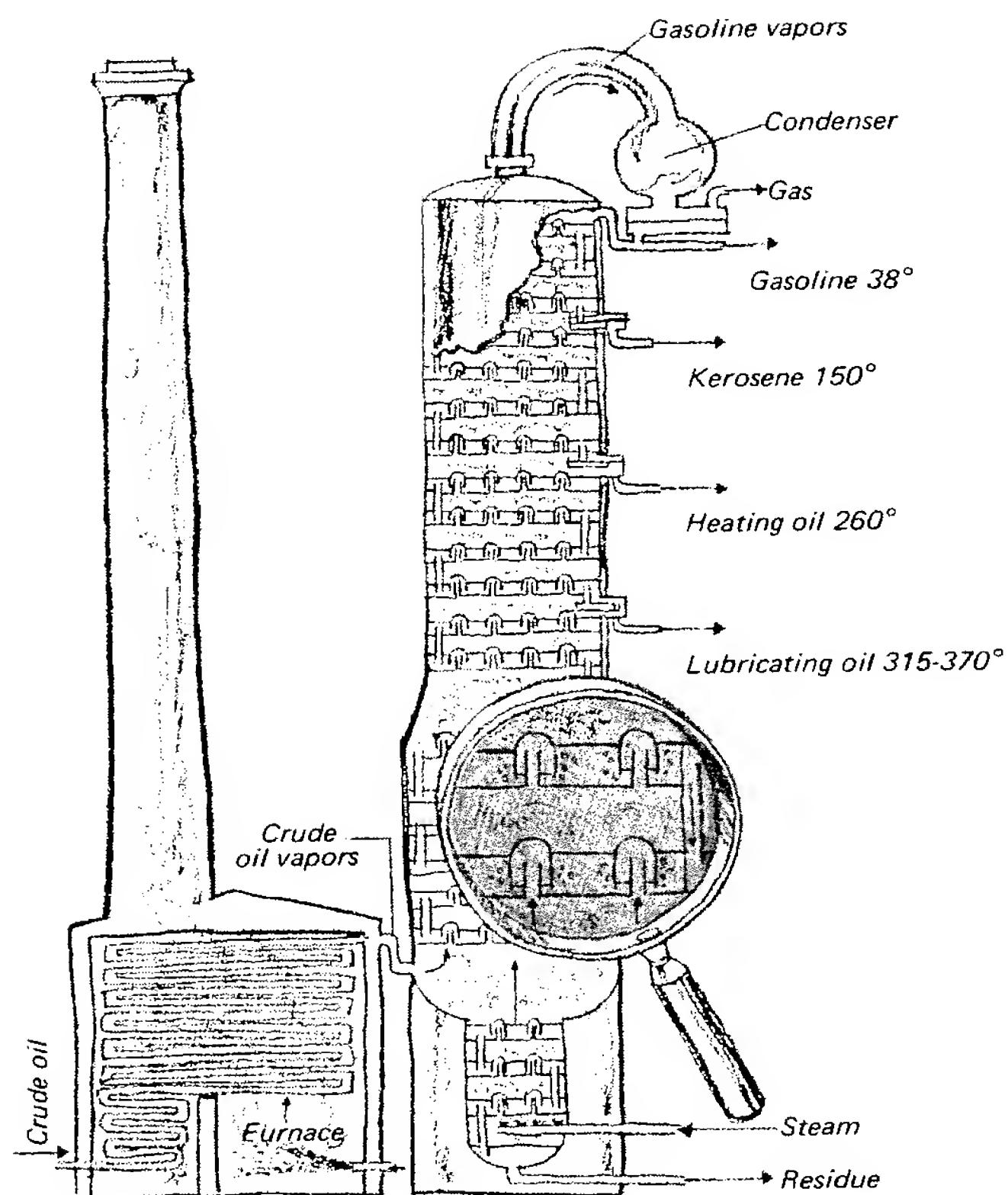
FIGURE 12-2

Fractional distillation of crude oil. Oil heated to about 425° C in the furnace vaporizes when it enters the tower at the right. The vapors rise through a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. The fraction of highest boiling point is drawn off at the bottom as a residue. It is heavy fuel oil. In modern refineries these fractions, which still consist of mixtures of hydrocarbons, are further processed.

SOLUTIONS OF SOLIDS IN LIQUIDS

12.8   The Effect of Temperature on the Solubility of Solids

When a solid dissolves in a liquid, a change in the physical state of the solid analogous to melting takes place. Energy is absorbed in overcoming the forces which hold the molecules, atoms, or ions in their lattice positions in the crystal. This is an endothermic change that accompanies the dissolution of all crystalline solids in liquids. The physical process of solution is often accompanied by a second change, that of a chemical reaction between the solute and the solvent. This second change is commonly exothermic in character. If the heat evolved in the chemical

change is greater than that absorbed in the physical change, the heat of solution is negative; i.e., the net process is exothermic. In other cases the heat of solution is positive; i.e., the net process is endothermic (see Section 6.5). Furthermore, heat is either absorbed or evolved during the process of crystallization of a solid from solution, a process opposite to that of a solid going into solution.

The opposed processes of dissolution and crystallization under conditions of equilibrium between a solid and its saturated solution may be represented by the following systems:

(1) Exothermic: solute + solvent $\rightleftharpoons$ solution + heat (negative heat of solution)
(2) Endothermic: solute + solvent + heat $\rightleftharpoons$ solution (positive heat of solution)

The addition of heat (a rise in temperature) in system (2) causes more of the solute to dissolve; the added heat is absorbed by the system when the equilibrium shifts to the right. This is the case with most solid-liquid solutions. In system (1) the solubility decreases with a rise in temperature.

The dependence of solubility upon temperature for a number of inorganic substances in water is shown graphically by the solubility curves in Fig. 12-3.
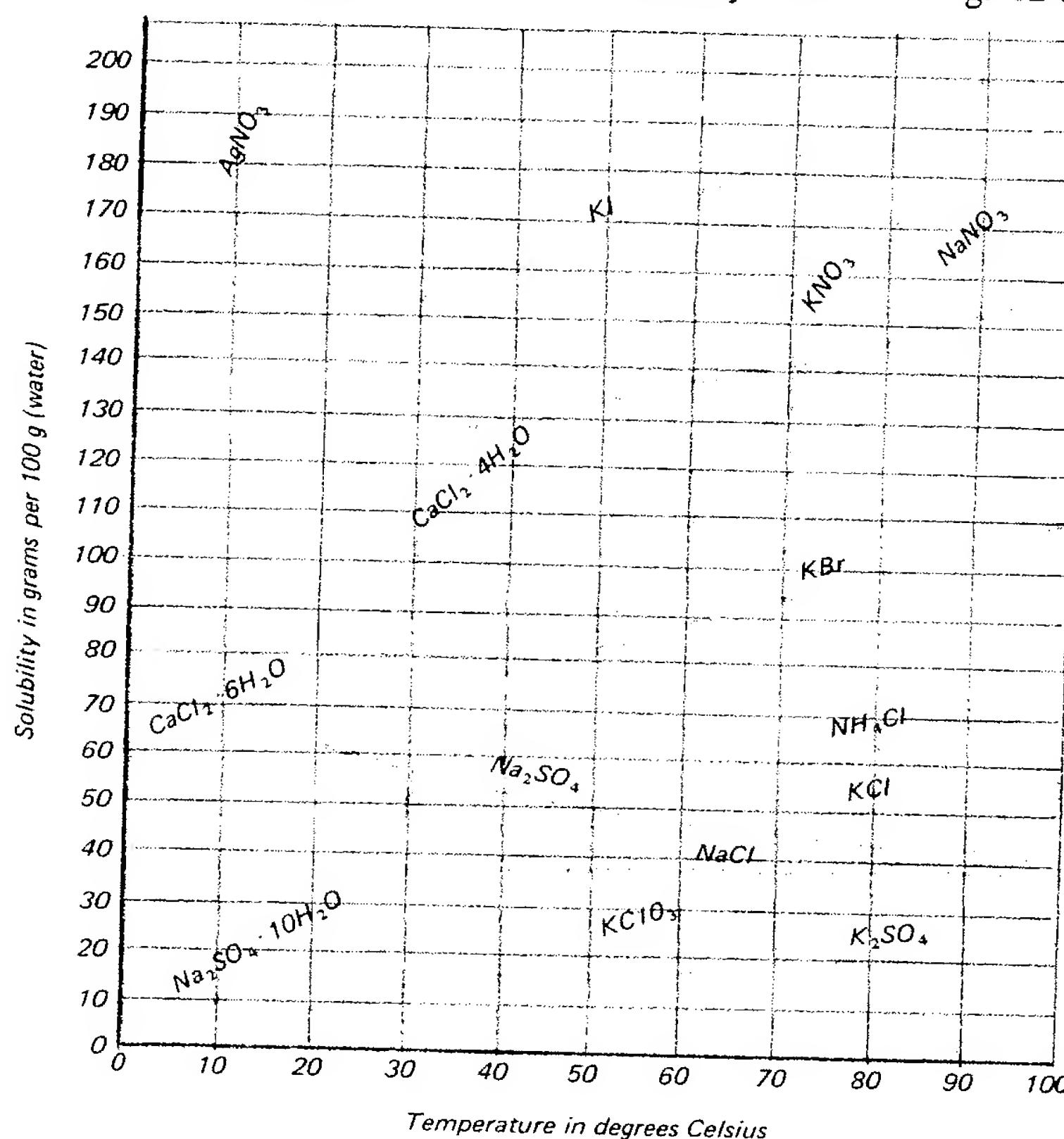

Graph showing the effect of temperature on the solubility of several inorganic substances.

Note that the solubility of sodium chloride increases very slightly with a rise in temperature whereas that of potassium nitrate increases greatly. A sharp break in a solubility curve indicates the formation of a compound whose solubility is different from that of the substance from which it was formed. When $Na_2SO_4 \cdot 10H_2O$ (Glauber's salt) is heated to 32.4°, it loses its water of hydration and forms the anhydrous salt, Na_2SO_4. The curve up to 32.4°, the **transition point,** represents the effect of a rise in temperature upon the solubility of $Na_2SO_4 \cdot 10H_2O$ and the curve for temperatures above this point represents the effect of a rise in temperature upon the solubility of Na_2SO_4.

12.9   Saturated Solutions

It was noted in Section 12.1 that sugar dissolves in water at a given temperature until the point of saturation is reached, and the solution is said to be **saturated.** When more sugar is added to a saturated solution, it falls to the bottom of the container, and it appears that the dissolving process stops. Actually, molecules of sugar continue to leave the solid under the solvent action of the water and go into solution. However, as the molecules of sugar in solution move about by diffusion, some of them collide with the solid on the bottom and take up positions in the crystal lattice. This process of crystallization is the opposite of dissolution. If enough molecules return to the solid state from the saturated solution, the process of crystallization just counterbalances that of dissolution, and we have a state of dynamic equilibrium. The same reasoning holds when no crystals are formed—for example, ether in water. **A saturated solution is one which is in equilibrium with the undissolved solute.** If a crystal of imperfect shape is placed in a saturated solution of the crystalline material, it will slowly "mend" its shape by loss of particles to the solution and gain of particles from the solution. This is experimental evidence that a saturated solution in contact with its solid solute is a system in dynamic equilibrium.

12.10   Unsaturated Solutions

An unsaturated solution contains less solute dissolved in a given quantity of solvent than would be the case for a saturated solution. Excess solute will not exist in an unsaturated solution. Instead the solute dissolves and the concentration of the solution increases until either the solution becomes saturated or all the solute has gone into solution.

12.11   Supersaturated Solutions

When saturated solutions of solid solutes are prepared at elevated temperatures and then permitted to cool, the excess solute usually separates from the solution by crystallizing. However, if a saturated solution is prepared at an elevated temperature and excess solute removed, crystallization often does not take place if the solution is allowed to cool undisturbed. **The solution contains more of the solute than it does when it is in equilibrium with the undissolved state and is called**

a supersaturated solution. Such solutions are metastable (unstable) systems. Agitation of the solution or the addition of a "seed" crystal of the solute may start crystallization of the excess solute; after crystallization, a saturated solution in equilibrium with the crystals of solute remains.

Gases also form supersaturated solutions. For example, a bottle of a carbonated beverage may not liberate the excess carbon dioxide when opened, but if it is shaken or stirred, it does. A supersaturated solution of a gas in a liquid is prepared either at low temperature, or under pressure, or both ways.

Rate of Solution 12.12

Rate of solution pertains to the amount of solute entering the solution per unit of time. It depends upon several factors. First, more soluble substances dissolve more rapidly than less soluble ones. Second, because the dissolution of a solid can take place only at the surface of the particles, the more finely divided the solute is (the greater the surface area per unit mass of the substance), the greater will be its rate of solution. Third, the rate of diffusion of the molecules away from the solid solute is relatively slow and so the solution in the immediate vicinity of the solid phase approaches the saturation concentration. Stirring or shaking the mixture brings unsaturated solution in contact with the solute and thus increases the rate of solution. Fourth, heating results in convection currents which produce the same effects as agitation of the mixture, and heating also usually increases the solubility of the solid.

THE CONCENTRATION OF SOLUTIONS

Standard Solutions 12.13

The solubility of a pure solid substance in a pure solvent at a given temperature is a quantitatively definite physical property of the substance. The solubility of sodium chloride is 35.8 g per 100 g of water at 20°; that of NaF is 4.2 g; and that of silver bromide is 0.00002 g. A general idea of relative solubilities is conveyed by use of the terms **quite soluble, moderately soluble,** and **slightly soluble** or **insoluble.** Strictly speaking, no substance is absolutely insoluble, although for all practical purposes many substances appear to be so. The relative concentrations of solutions may be expressed by the terms **dilute** (containing a small proportion of solute) and **concentrated** (containing a large proportion of solute).

Chemists often work with unsaturated solutions of known concentrations, which are called **standard solutions.**

The concentrations of solutions may be expressed in a number of ways. It is important that the methods of expressing concentrations of solutions be thoroughly mastered.

Percentage Composition 12.14

One method of expressing concentration in physical units involves the weight of solute in a given weight of solvent; for example, 1 g of NaCl in 100 g of water.

MODERN SUPERABSORBENT POLYMER TECHNOLOGY

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Andrew T. Graham

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product particle size distribution. The presence of extremely fine particles ("fines"), typically less than 140 μm in diameter, has been unacceptable in the commercial product for diapers. Several means of converting the fine material to other saleable products, or recycling it in the current process, are described in section 3.2.7.

Technology for preparing products with a higher degree of crosslinking on the surface has long been known and is useful as a means of increasing absorption rate. More recently, superabsorbent products with an improved combination of swelling capacity and absorption under a compressive load (see Chapter 5) have been realized using such structured particle technology. Often, a crosslinker is added to the desired particle size distribution and is reacted to yield the structured product. Patents describing the chemistry indicate that a variety of blenders and heating devices are suitable.

Most unit operations in a commercial superabsorbent polymer plant have the potential to release small quantities of acrylic acid, other organics, or particulates to the environment. For example, as the polymerization reactor is filled with liquid, the vapor in the vessel is displaced and must be treated to remove any acrylic acid vapor before being released to the environment. The hot, moist gel fed to a dryer may release small quantities of unreacted acrylic acid into the surrounding air, creating an industrial hygiene problem for plant personnel. Also, in addition to containing unreacted acrylic acid, the air used in a through-circulation dryer to transfer heat to the polymer may contain fine particles of dry polymer product. These would need to be removed before the air from the dryer is returned to the environment. Enclosing the operations allows the air to be treated to remove contaminants. All major U.S. and European manufacturers treat their air streams to reduce emissions.

3.2.2. Raw Material Preparation

In this step, the ingredients to be added to the reactor, acrylic acid, water, an optional graft substrate, for example, starch[12] or poly(vinyl alcohol) solution, and a base, are prepared,[14-18] usually in a batch-wise fashion. The decisions taken in this step affect how the rest of the process operates, particularly the polymerization reaction, and are the primary determinants of the network structure of the dried particle. Monomer concentration (polymerization solids), the degree of primary crosslinking, and percent neutralization of the final product are typically set in this step. The degree of crosslinking affects the final product performance properties, swelling, and modulus (see Chapter 5). The degree of neutralization also affects the swelling behavior of the final product. However, when the pH of the product is to be maintained in a range safe for contact with human skin,[18] the most desirable percent neutralization is from 60 to 90 mol%. The monomer concentration in the reaction step determines, throughout the reaction, the demands on the heat removal system and the rheology of the partially polymerized hydrogel. The modulus, swelling capacity, and amount of extractable polymer of the polymer gel, determined in the polymerization step, affect its subsequent handling.

The primary monomer is high purity acrylic acid alone or in combination with its partial sodium or potassium salt. Typical impurities in acrylic acid include the

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The formation of storage has long bee dependent on the am has been thoroughly by heating[21] at tempe Acrylic acid dimer, into the polymer bac during the drying of bone and 1 mer of ε heating temperature monomer. To minim quantity of dimer in

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dimer of acrylic acid, the polymerization inhibitor MEHQ, and small amounts (ppm) of several other materials. In at least one case, purification by distillation, just prior to use, of the acrylic acid monomer removes the inhibitor MEHQ and removes acrylic acid dimer to prevent the formation of β-hydroxypropionic acid.[19]

The formation of diacrylic acid (acrylic acid dimer) from acrylic acid during storage has long been known. The rate of formation is temperature dependent and dependent on the amount of moisture present as an impurity in the acrylic acid; this has been thoroughly documented.[20] The dimer of acrylic acid can be decomposed by heating[21] at temperatures from 120° to 220°C, yielding 2 mol of acrylic acid.[22,23] Acrylic acid dimer, because it contains a double bond, may also be incorporated into the polymer backbone.[20] A portion of the incorporated dimer may be cleaved during the drying of the polymer and apparently leads to 1 mer of polymer backbone and 1 mer of acrylic acid. The percentage of dimer cleaved depends on the heating temperature.[24] The unreacted acrylic acid is detectable as residual monomer. To minimize the amount of acrylic acid detectable in the product, the quantity of dimer in the acrylic acid feed is generally minimized.

Acrylic acid containing dimer may be treated with strong aqueous base prior to polymerization.[20,24,25] The reaction product of dimer hydrolysis is 1 mol of acrylate ion and 1 mol of β-hydroxypropionic acid. The β-hydroxypropionic acid may be trapped in the polymer matrix (although not polymerized) and will not be detected as residual acrylic acid by standard techniques (see Chapter 4, section 4.4.1). The β-hydroxypropionic acid may also be dehydrated to acrylic acid during a heating step.[26] However, it is our experience that higher temperatures are required to dehydrate β-hydroxypropionic acid than are required to thermally cleave acrylic acid dimer incorporated in the polymer backbone.

MEHQ is added to acrylic acid during its manufacture and acts in combination with oxygen as a polymerization inhibitor during storage and handling. It is normally present in acrylic acid at 200 ± 20 ppm. MEHQ, in combination with the thermal initiator persulfate ion can contribute to color formation in the final product.

A primary crosslinker is used at concentrations of about 500 ppm to 1 wt% (0.01–0.2 mol%), based on acrylic acid, so that the reaction product will be a crosslinked gel of the desired swelling capacity. Suitable divinyl crosslinkers include trimethylolpropane triacrylate, methylenebisacrylamide, diethyleneglycol diacrylate, triallylamine, allyl methacrylate, tetraallyloxyethane, and the like.[17,18,27–29] The choice of crosslinker,[30] through the crosslinker reactivity ratio, in combination with other polymerization parameters, will affect the amount of soluble polymer produced. Additional minor components in the reaction mix include chelants and dispersants,[28] or surfactants,[18] to aid in the solubilization of the hydrophobic crosslinkers.

Lower monomer concentrations have been chosen to improve end-use properties[18,31] or to facilitate handling. However, operating at the highest monomer concentration possible improves reactor throughput, in mass of product per unit time, and economics. However, as monomer concentration increases, a higher adiabatic temperature rise is possible (Fig. 3.2). Thus, higher monomer concentrations, in combination with temperature-sensitive initiator systems, lead to higher tempera-
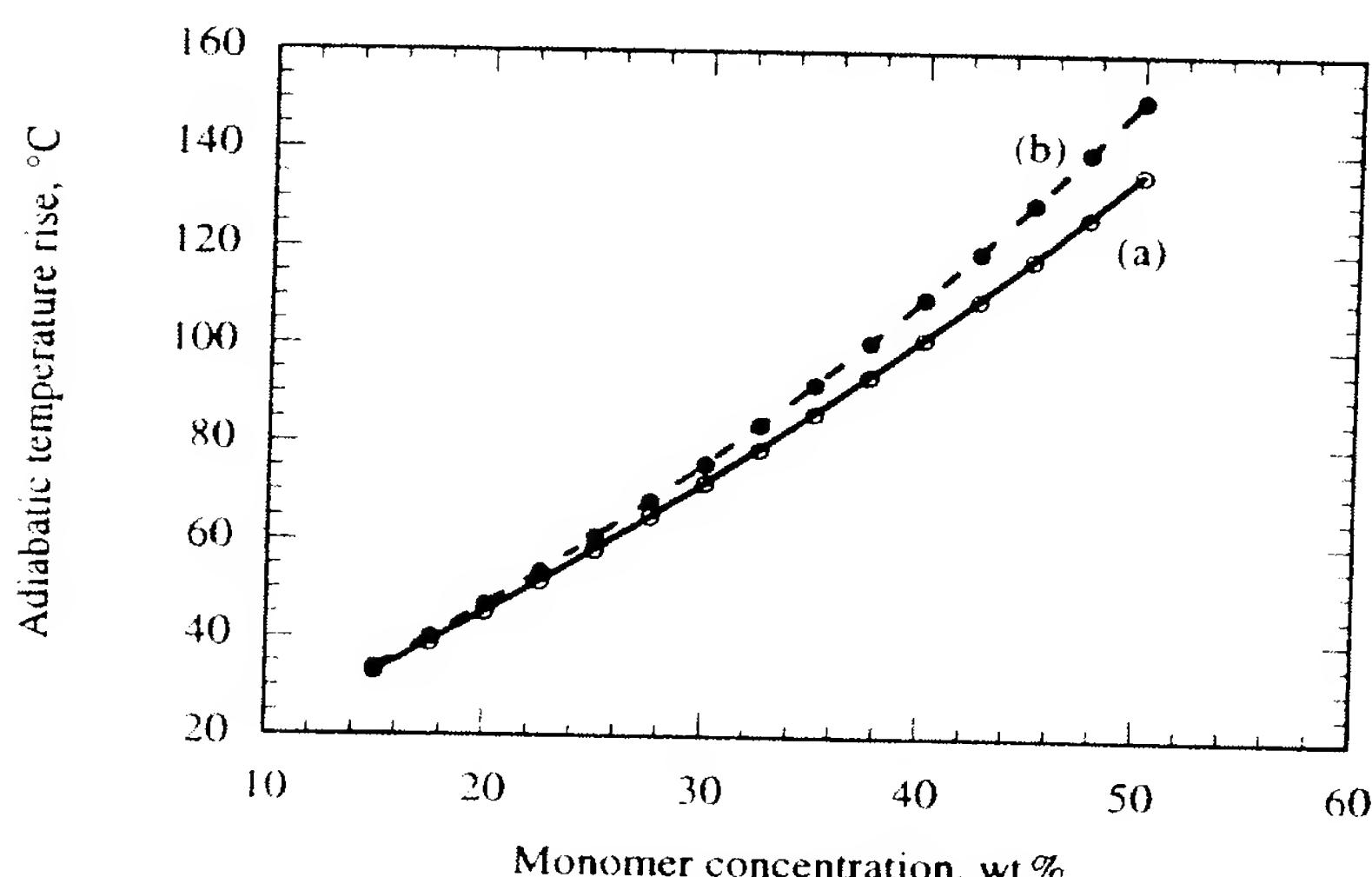
Figure 3.2. Adiabatic temperature rise for polymerizations of crosslinked partially neutralized acrylic acid as a function of monomer concentration. The heat of polymerization of acrylic acid was taken as 77.4 kJ/mol, and the heat capacity of the polymer was taken as either 0.50 **(a)** or 0.35 cal/g°C **(b)**.

tures and higher initiation rates near the end of the polymerization when monomer concentration decreases. As a net result, lower molecular weight chains are produced near the end of the polymerization. If the crosslinker concentration is constant or decreasing, which depends on the relative reactivity of the crosslinker and the monomer, the shorter chains are less likely to be crosslinked into the network structure. Therefore, larger quantities of undesirable[31] extractable polymer (lower molecular weight polymer, not crosslinked into the network structure) are produced toward the end of the polymerization. Commercially useful monomer concentrations range from about 15% to 30% for the polymerization of acrylic acid[12] and from 30%–43% for the polymerization of partially neutralized monomer.[16,17,25,28,29,32,33]

The degree of neutralization (mole basis) used for polymerization ranges from 0% (unneutralized)[31,34,35] to 80%. When acrylic acid is polymerized, the polymer is subsequently neutralized to an extent of 50%–80%, most typically from 60% to 75%, by adding a solution of sodium hydroxide or sodium carbonate to the acidic gel polymer. At the commercial scale, neutralization of the monomer may be accomplished either by simply adding the aqueous base to the acid monomer or by more involved processes. In one specific process[25] the monomer is neutralized to greater than 100.1 mol% and held at that composition for up to 2 hours to hydrolyze acrylic acid dimer to β-hydroxypropionic acid.[19,25] The pH of the monomer mix must be greater than about a pH of 12 to effectively hydrolyze the acrylic acid

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50   60

wt %
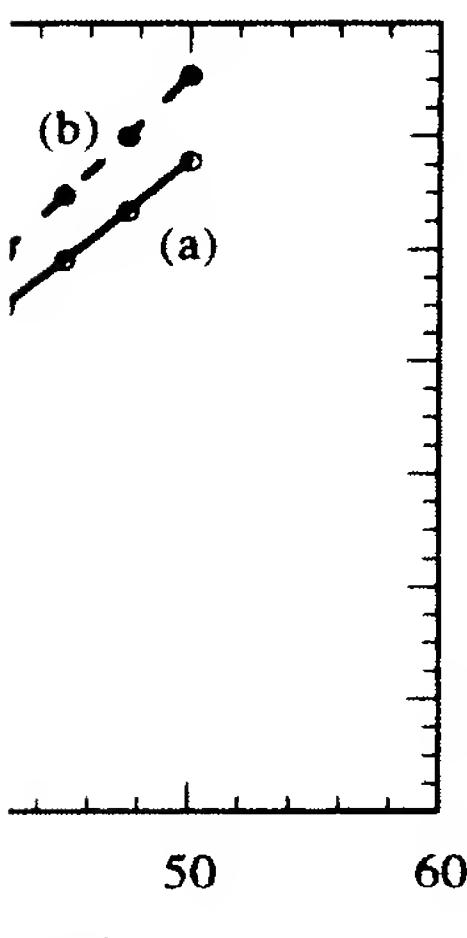
osslinked partially neutralized
polymerization of acrylic acid
was taken as either 0.50 (a) or

nerization when monomer
ar weight chains are pro-
nker concentration is con-
vity of the crosslinker and
osslinked into the network
xtractable polymer (lower
twork structure) are pro-
ercially useful monomer
polymerization of acrylic
artially neutralized mono-

olymerization ranges from
olymerized, the polymer is
st typically from 60% to
m carbonate to the acidic
the monomer may be ac-
the acid monomer or by
nonomer is neutralized to
up to 2 hours to hydrolyze
pH of the monomer mix
ydrolyze the acrylic acid

dimer.[24] This process results in a reduction in the residual monomer content of the final product.

Several orders of addition of reactants are possible, including the order specifically described earlier in discussing the neutralization process. The order of addition of ingredients may also be adjusted to accommodate factors such as crosslinker solubility or crosslinker sensitivity to hydrolysis. The crosslinker may be added to the acrylic acid prior to neutralization or to the fully neutralized monomer mix. If desired, the oily crosslinker may be dissolved in a portion of the acrylic acid prior to addition of the mixture to the balance of the neutralized monomer mix. Other orders of addition are described in the examples of the references of this section. After preparation, the monomer mix is moved to the polymerization step.

3.2.3. Polymerization Vessels and Systems

In the polymerization process, the monomer mix prepared in the previous process step is converted to a hydrated gelatinous rubbery polymer (hydrogel) with the evolution of heat. The polymerization vessel used for this process has substantially different requirements placed on it compared with a vessel for a liquid system because of the rubbery, semisolid nature of the crosslinked polymer hydrogel. In liquid systems, mixing in a reaction vessel is often of primary concern as a means of both uniformly mixing reactive ingredients and improving heat transfer required to maintain a uniform temperature in a vessel. However, essentially no mixing can take place after gelation, which occurs at only a few percent conversion, because of the high monomer concentrations, the high molecular weights achieved, and the presence of crosslinker.

The temperature increases in a reaction system if the rate of heat generation (rate of reaction) is faster than the rate of heat removal. Adiabatic or nearly adiabatic polymerizations of acrylic acid or partially neutralized acrylic acid can be very rapid, taking only 10–30 min to go from a few percent conversion to over 90% conversion (Fig. 3.3). This situation is favorable economically because it permits a high space–time yield for the capital dollars invested in reaction equipment. The kinetics of adiabatic polymerizations of acrylamide[36] and methyl methacrylate[37] have been reported and are similar in many features to those observed for acrylic acid or partially neutralized acrylic acid (see Chapter 2). Smaller molecular weight at high conversion (and higher temperature) results from lower monomer concentration, increased probability of chain transfer reactions, and increased initiation rate from the thermally activated initiators used for the polymerization. Therefore, to control the temperature of polymerizations with relatively large adiabatic temperature rises, and to avoid polymer degradation at high temperatures,[18,31] an efficient means of heat removal is required. However, the ability to remove heat is also affected by gelation at low percent conversion. When the surface-to-volume ratio is low, efficient mixing is required to transfer heat to a cooling surface such as a reactor wall.

Several polymerization systems have solved these problems. In one case, polymerization of acrylic acid is conducted at only about 20 wt% acrylic acid, thereby reducing the need for heat removal by limiting the total heat released. Also, the